Further X-ray studies of Carbonaceous and Bituminous Materials

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Abstract.

Fusain, graphitic anthracite, fibrous and non-fibrous peats and elaterite were examined by the X-ray diffraction method.

Fusain gives the carbon and ash spacings with the interspaces fairly clear. There is also evidence in the diagram of the fibre pattern. The graphitic anthracite shows well-defined halos of carbon and ash. There is no evidence of colloidal state in anthracite—either in carbon or in ash. The carbon seems to be here (as also in fusain) in a free state. The prominent ash rings in both fusain and anthracite have been ascribed to SiO_2 and Al_2O_3.

Fibrous peat gives a fibre pattern and the pattern given by the ordinary variety shows the presence of colloidal state. From a parallel relationship of the spacings given by peat to those of the coals it is suggested that there is a close relationship between peat and coal, the difference between the two being *mainly* one of structure, rather than of composition.

Elaterite, an organic mineral in association with coal seams gives a number of rings and on comparing the spacings with those for the higher members of the paraffin series, a close identity is found. Elaterite seems to be a mixture of the higher members of the paraffin series.

1. *Fusain.*

In a recent paper by the author [1] it was pointed out that while durain and vitrain may be considered as the distinct

[1] C. Mahadevan, Indian Journal of Physics, Vol. IV, pp. 78-97, 1929.

coal types, fusain (or mineral charcoal) was known to be mostly free carbon. Whether compact or friable, they show the fibrous nature [2] persistently, these being due to the preservation of their original cellulosic structure. Fusain blackens the fingers when handled. The absence or scarcity of water (which is surmised to act as a thermostat in the natural process of coalification) seems to account for the formation of fusain.

Fusain was examined by the X-ray diffraction method described in the earlier paper (*loc cit.*). It is seen that the pattern obtained shows a number of rings, much like durain, but with this difference, that the interspaces between the various halos in fusain are comparatively clear and in addition, an unmistakable evidence of the fibre structure is obtained as seen from localised spots of increased intensity along the stonger halos of the diffraction pattern. Spacings for the various halos were calculated and it is seen from Table I that most of the rings can be ascribed to carbon.

The absence of general scattering between the various halos finds explanation from the fact that volatile materials and moisture are almost entirely absent in fusain. The rings are all comparatively well defined testifying to the fairly coarse nature of carbon and ash particles. The fibrous structure of the original organic matter is still preserved in fusain which manifests itself as the localised spots of intensity in the strong halos of the X-ray pattern.

Besides the carbon spacings, there are other halos present also. Ash being the main associate of carbon in this coal, the fusain was ignited in a platinum crucible over Mecker burner for ten hours until constancy of weight was obtained. An X-ray diffraction pattern of this ash was taken and the results tabulated (Table II). The first ash ring corresponds to a spacing of 4·28 A. U. and the second, to 3·49 A. U.

[2] C. S. Fox, Presidential Address, Geology Section, Ind. Sc. Congress, Madras, 1929.

From chemical analyses, it is now well established that SiO_2 and Al_2O_3 are the principal constituents of coal ash, though, of course, other mineral matter may be present in smaller quantities. To see if the ash rings would be attributable to SiO_2 and Al_2O_3, calculations of the spacings for the most prominent faces of these minerals were made from the equation [3]

$$d=\frac{hx_1+ky_1+lz_1-1}{\sqrt{\frac{4}{3}(h^2+hk+k^2)+(l/c)^2}}$$

and the values obtained are tabulated (Table III).

It is seen from a comparison of Tables II and III that the two prominent halos in ash correspond very nearly to the spacings deduced for SiO_2 and Al_2O_3. The superposition of the prominent carbon halo (3·38 A.U.) over the ash halo is clearly made out in the original fusain pattern. In the carbon free ash diagram, it is seen to stand out clearly where its true dimension can be made out without much ambiguity.

As was seen in the case of durain, a halo with larger spacings ($\theta=12°25'$) is observed in the fusain patterns also.

2. *Graphitic Anthracite.*

Graphitic Anthracite is a mineral obtained through metamorphism of bituminuous coals by igneous agencies as a result of which the volatile gases and moisture are driven out and carbon in a free state exists in abundance. More than 90% of the substance is carbon and a small amount of ash exists in association with this carbon. It is hard and brittle with a submetallic to metallic lustre and of conchoidal fracture.[4]

[3] A. W. Hull, Phys. Rev., Vol. X, p. 678, 1917.

[4] T. E. Thorpe, A Dictionary of Applied Chemistry, Vol. 2, p. 160 (Longmans Green & Co.) See also A Text Book of Mineralogy—E .S. Dana. (John Wiley and Sons, N. Y.) 1922.

The X-ray diffraction pattern of graphitic anthracite is very characteristic (Table IV). The halos are all quite sharp and well defined and the interspaces between them, perfectly clear. The complete absence of volatile matter and the presence of free crystalline carbon occasion this characteristic diffraction pattern. Examining the various halos obtained for the graphitic anthracite, it is found that there are the two prominent carbon rings. There is also the halo at small diffraction angle ($\theta = 11^\circ\ 25'$).

Of the halos ascribable to ash, the inner one with $a = 4{\cdot}44$ A.U. corresponds closely with the value $a = 4{\cdot}45$ A.U. derived for SiO_2 for the face (001) from Hull's formula.[5] It is also very easily seen that the spacing $a = 3{\cdot}54$ A. U. for the basal plane (001) of Al_2O_3 overlaps the carbon ring at 3·38 A.U.

The other rings with smaller spacings for the ash are fairly sharp in graphitic anthracite. In durain (and to some extent in fusain) these rings were rather diffuse and it was inferred from this evidence (as also supported by other researches) that part of the ash in bituminous coals was in colloidal associations.[6] The obvious conclusion from the fact of the observation of these small spaced ash rings occuring fairly well defined in anthracite is that during the process of metamorphism, they have altered their dimensions to coarser particles.

3. *Fibrous and Nonfibrous Peat.*

The two kinds of peat—the fibrous and nonfibrous—were next studied by the X-ray diffraction method. The ordinary peat is known to be a colloid.[7] In this variety of peat, there are only two halos at spacings equal to 3·70 A.U. and 2·33 A.U. both being diffuse and ill-defined. The former of these

[5] A. W. Hull, Phys. Rev., *Loc Cit.*

[6] C. Mahadevan, Ind. Jour. Phys., *Loc Cit.*

[7] R. H. Bogue, Colloidal behaviour, p. 504. (McGrawhill Book Co.) 1924

corresponds to a prominent halo at a spacing 3·67 Å.U. whereas the latter appears to be an average effect of the three other halos present in the fibrous variety (Table V). This general diffuseness of the halos in the ordinary peat strongly supports the view that it is mainly of a colloidal nature.

In the fibrous peat, there are localised spots of intensity characteristic of a fibrous structure and other faint but fairly well defined halos. It is well known that peat is a transition stage between unaltered vegetable debris and true coals, the differences between the former and later being the want of homogeneity, presence of vegetable structures only partially altered, etc.[8] It is of great interest to see on a comparison of the spacings for durain[9] and fibrous peat and vitrain and nonfibrous peat (Table V) that all the rings present in true coals (except those due to ash) are also present in the corresponding peats. It should however be noticed that there is a small uniform increase in the spacing of each ring in the case of peats. This difference in X-ray pattern may be attributed to either a small difference in the respective chemical constitutions or to a structural difference but it is very hard to reconcile this close similarity with any chemical transformation of a serious nature in the process of the formation of coal from peat.

It is well known that there is a gradual falling of the density as we proceed from anthracite to the earlier members (anthracite 1·4-1·8, bituminous coal 1·2-1·5, lignite 1·1-1·4). The density of coal is far too high to be accounted for only by the larger percentage of ash present therein. The low density of peat falls in a line with the observed uniform increase in the spacings of the materials. This suggests a great similarity between peat and coal in their chemical constitution, the real difference being probably due to the closeness of packing. It

[8] E. S. Dana, Text-book of Mineralogy, *Loc Cit.*

[9] C. Mahadevan, Ind. Jour. Phys., *Loc Cit*, p. 95.

is intended to treat the peats to the solvent action of organic liquids and study the products also.

4. *Elaterite.*

Elaterite, popularly known as mineral Caoutchouc is a soft elastic mineral adhering to the fingers, found in association with coal seams and oil deposits. Johnston[10] analysed it but left the constitution in doubt. Later attempts in this direction have not been more successful. It appears to be made up of hydrocarbons, thus possessing a constitution similar to that of the well known organic mineral ozocerite with a very small portion (less than 2%) of oxygenated insoluble material.

The X-ray pattern for elaterite is very interesting. One well defined and extremely intense halo and several sharp halos of varying intensity are obtained on the photographic plate resembling very much a paraffin wax diagram. Surmising that the mineral may consist of the higher members of the aliphatic series, the calculated spacings (Table VI) were compared with the X-ray data for the higher members of the long chain hydrocarbons (Table VII).[11] It is seen that the spacing 3·9 A.U. which is the most intense halo in the diagram is also the spacing common to most of the members of this series. It is also seen that corresponding to almost all the spacings in the aliphatic hydrocarbons group (higher members —Table VII) we find identical spacings in elaterite. It seems obvious from the data that elaterite consists almost entirely of the higher members of the aliphatic hydrocarbons.

The halo with 6·65 A.U. may be due to the trace of the oxygenated insoluble matter or to a harder radiation corresponding to one of the intense halos in the diagram.

[10] Johnston, Phil. Mag., 13, p. 22. 1838.

[11] International Critical Tables, Vol. I, p. 347, 1926.

5. *Experimental.*

The same type of the shearer tube with aluminum cathode and copper target described in the earlier paper (*loc cit.*) was used with Waran's pumps for high vacuum and "Cenco-Hyvac" for initial backing. The high tension for these experiments was supplied by an oil cooled transformer with an alternate spark gap of 3·5 inches. The secondary current was about 6 mil-amps. and the exposure varied from 4 to 9 hours according to the substance.

The camera used was the same as that described in the earlier paper except that the hole of the camera was made much smaller to facilitate a greater resolution. The other experimental details have been enumerated before and do not require to be repeated in this paper.

The samples of fusain and graphitic anthracite were treated with pyridine but gave very little extract.

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TABLE I.

Fusain.*

No. of rings.	θ	$a = \frac{\lambda}{2 \sin \frac{\theta}{2}}$	Remarks.
1	12°21′	7·16	Fair spots of localised intensity.
2	20°45′	4·29	Strong.
3	26°19′	3·37	Strong. Crystal powder pattern superposed.
4	35°21′	2·72	Very fair.
5	41°5′	2·19	Do.
	42°24′	2·13	Faint, diffuse.
	49°35′	1·84	Very faint, diffuse.
8	53°57′	1·75	Do.

Table II.

Fusain Ash.

No. of rings.	θ	$a = \frac{\lambda}{2 \sin \frac{\theta}{2}}$	Remarks.
1	20°32′	4·44	Very fair.
2	25°29′	3·49	Strong.
3	33°39′	2·65	Fair.
4	40°53′	2·20	,,

Table III.

Calculated spacings for SiO_2 and Al_2O_3.

Substance planes.	100	010	001
SiO_2	4·25	4·25	4·45
Al_2O_3	4·11	4·11	3·54

Table IV.

Graphitic anthracite.

No. of rings.	θ	$a = \frac{\lambda}{2 \sin \frac{\theta}{2}}$	Remarks.
1	11°25′	7·73	Fair.
2	20°2′	4·44	Very fair.
3	26°29′	3·36	Strong.
4	33°39′	2·67	Fair.
5	35°10′	2·55	,,
6	42°44′	2·11	,,

TABLE V.

Peats.

	Fibrous variety.			Non-fibrous variety.		
No. of rings.	θ	$a = \frac{\lambda}{2 \sin \frac{\theta}{2}}$	Remarks.	θ	$a = \frac{\lambda}{2 \sin \frac{\theta}{2}}$	Remarks.
1	15°5′	5·83	Very fair.	...	......	...
2	24°11′	3·67	Strong.	23°59′	2·70	Strong and diffuse.
3	31°3′	2·88	Fair.	...	......	...
4	36°45′	2·44	,,	...	......	...
5	41°56′	2·01	,,	38°32′	2·33	Fair and diffuse.

TABLE VI.

Elaterite.

No. of rings.	θ	$a = \frac{\lambda}{2 \sin \frac{\theta}{2}}$	Remarks.
1	13°0′	6·65	Faint.
2	20°57′	4·16	Very fair
3	22°28′	3·95	Very intense.
4	26°7′	3·41	Strong.
5	32°0′	2·79	Fair.
6	37°34′	3·39	Very fair.
7	42°6′	2·11	,,
8	47°22′	1·91	Fair.

TABLE VII. *

Long chain Compounds (Aliphatic hydrocarbons).

Formula.	d_1	d_2	d_3	d_4	d_5	d_6
$C_{17}H_{36}$	4·25	3·93	...	2·54	2·32	...
$C_{18}H_{38}\alpha$	......	4·0	...	...	...	...
$C_{18}H_{38}\beta$	4·58	3·80	3·66	2·61	...	2·05
$C_{19}H_{40}$	4·22	3·84	...	2·52	2·25	...
$C_{20}H_{42}\alpha$	......	3·9	...	...	...	...
$C_{20}H_{42}\beta$	4·63	3·82	3·61	2·59	2·12	2·03
$C_{21}H_{44}$	4·17	3·77	3·01	2·50	2·25	...
$C_{23}H_{48}$	......	......	...	...	...	...
$C_{24}H_{50}$	4·18	3·80	3·02	2·50	2·25	...
$C_{27}H_{56}$	4·17	3·77	3·01	2·51	2·25	...
$C_{31}H_{64}$	4·14	3·74	2·99	2·49	2·21	...
$C_{35}H_{72}$	...	......	...	...	...	...

* From International Critical Tables, Vol. I, p. 347 (1926).